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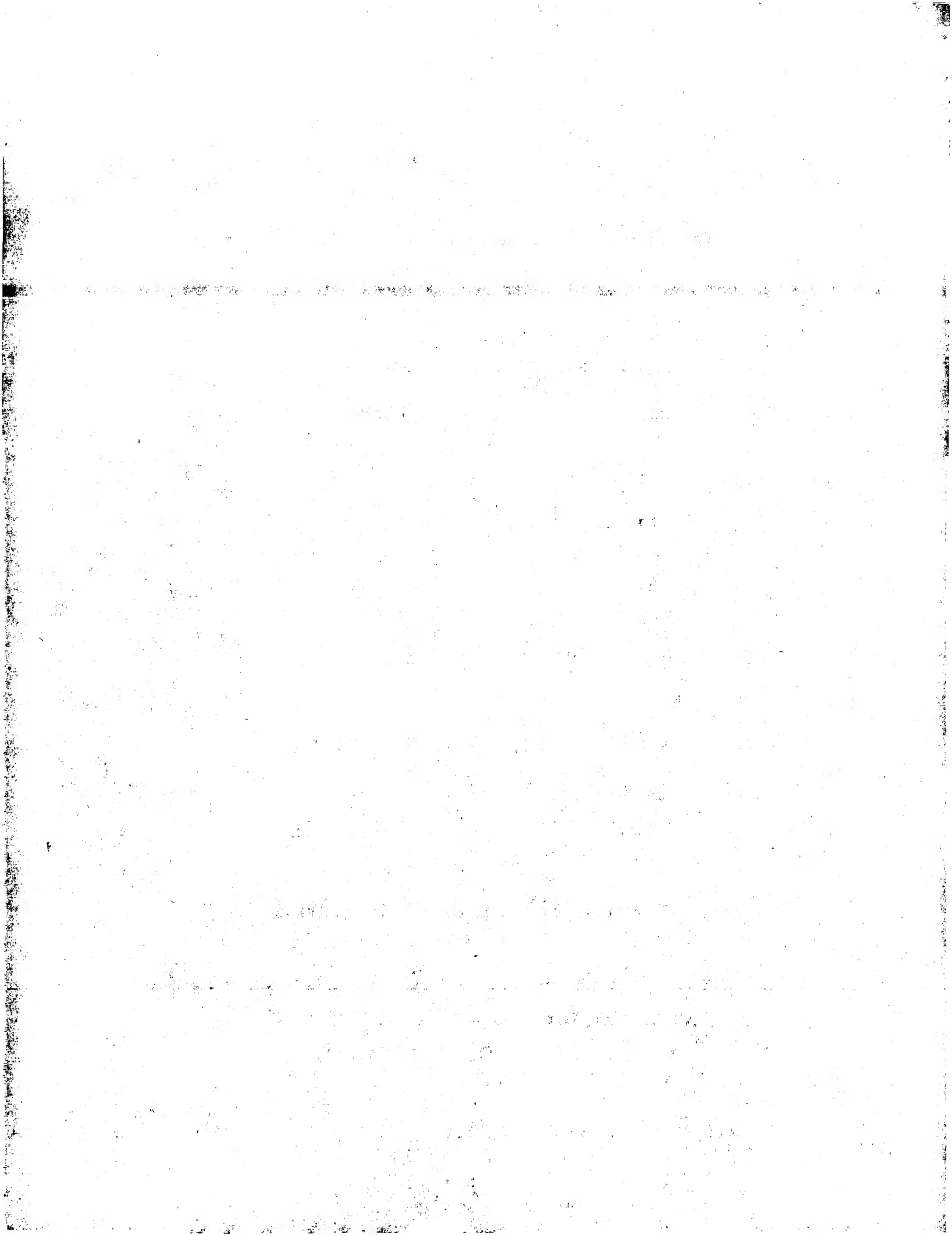
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(71) Applicants
Sanyo-Kokusaku Pulp Kabushiki Kaisha (Japan),
4-5 Marunouchi 1-chome, Chiyoda-ku, Tokyo, Japan
Mitsubishi Yuka Fine Kabushiki Kaisha (Japan),
No 11-41 Akasaka 1-chome, Minato-ku, Tokyo, Japan

(72) Inventors
Hideki Tani,
Makoto Arai,
Takayuki Sasaki,
Kazuhide Hayama,
Akira Yamashita

(74) Agent and/or Address for Service
F. J. Cleveland,
40-43 Chancery Lane, London WC2A 1JQ

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(54) Recording sheets

(57) A sheet for water base ink recording comprises a backing substrate including a surface layer obtained by ultraviolet or radiation curing of a composition composed mainly of an ultraviolet or radiation curing type resin optionally starting from a natural high-molecular substance and, optionally containing an ultraviolet or radiation curing type antistatic agent.

GB 2 151 945 A

SPECIFICATION

Recording sheets for water base ink and process for making the same

- 5 The present invention relates to a recording sheet adapted to be used with a water base ink, such for
example as a sheet of paper or plastic films, on which is recorded an image of high picture quality through
the application of the ink jet recording. 5
- In recent years, the ink jet recording has been increasingly used in facsimile machines, word processors
and terminal printers, etc., since it causes no noise, needs no procedures for development and fixation,
10 enables high-speed recording, and is capable of multi-colour recording. Development of ink jet recording is 10
now being concentrated on colour printers based upon the ink jet recording methods for the purpose of
making coloured, hard copies from colour displays.
- The ink jet colour printers have heretofore been used in a colour graphics field wherein seven colours
(yellow, magenta, cyan, red, green, blue, black) are used. In recent years, however, the development is now
15 being forwarded to high-resolution colour printers which give full-colour copies of high quality comparable 15
to that achieved by gravure printing or silver salt photography, the so-called pictorial colour copies.
- Ink jet recording is fundamentally advantageous in being capable of using plain paper, the so-called PPC
(Plain Paper Copies). However, satisfactory results are not yet obtainable if ordinary plain papers are used as
the sheets for ink jet recording especially for multi-colour recording. The sheets suitable for ink jet colour
20 recording or copying presently require the following properties:- 20
1. Ink dots are of a round shape, are not faded in colour, and make a sharp contrast to their circumferences,
thus leading to high resolution;
 2. Ink dots are high in both colour density and colour saturation;
 3. They absorb ink rapidly in a large amount, dry rapidly, and show good multi-colour recording
25 properties, by which, when ink dots are superposed upon each other, the outermost ink is prevented from 25
flowing out; and
 4. They show a dimensional stability with no fear of suffering curling, waving or deforming which may be
caused by recording.
- From the foregoing, it will be appreciated that a major technical problem is to obtain simultaneously the
30 properties of ink absorptivity dominating the speed of ink drying on the one hand and dot spreading 30
accompanied with low resolution on the other. Generally, as the ink absorptivity of a recording sheet
increases, the ink dot spreading increases so that the shape of ink dots is distorted, resulting in lowering of
resolution. In addition, an ink having the tendency to penetrate deeply into the paper layer leads to lowering
of colour density and colour saturation.
- 35 When using a multi-colour ink jet printer, the recording sheet used should have high ink absorptivity, since 35
the ink droplets of various colours are deposited onto the same or neighbouring portions thereof within a
very short time, otherwise unabsorbed amount of ink will flow, thus causing, at best an indistinct image and
at worst an unsightly smudge.
- Normal paper such as fine paper may be used as the ink jet recording sheet. In this case, however, the
40 various paper properties such as the degree of sizing, air permeability, density, smoothness, and 40
dimensional stability such as elongation in water, etc., should be monitored or selected depending upon the
recording systems involved, the conditions applied or the ink used. At the present time, however, it is not
practicable to make colour recording of high picture quality, now demanded, only through optimizing the
above-mentioned properties of the normal paper.
- 45 In addition to the foregoing, there is also a requirement to print or copy not only onto papers, but also 45
impregnated paper sheets, plastic films, synthetic paper sheets, and metal sheets, which are water-
resistant. Referring for instance to the increasing demand for colour displays for use with the computers for
personal use, it is desired to develop transparent films, which make ink jet colour recording possible, in order
to use hard copies with OHP (Overhead Projectors). However, any plastic films such as transparent polyester
50 films used as the OHP films cannot be applied for that purpose, since, unlike paper, they are hydrophobic 50
and, hence are of no ink absorptivity at all. This is also true for other substrates such as impregnated papers,
metalized paper, synthetic papers and metal sheets.
- As discussed above, some technical limits are placed on the development of ink jet recording sheets based
on such new substrate materials when it is attempted on the basis of the structural concept of the
55 conventional ordinary or coated papers. 55
- In view of the aforesaid considerations, the present invention seeks to provide sheets for the ink jet
recording, on which the images of high colour picture quality are printed by ink jet recording, and which are
based on substrate materials such as impregnated papers, metallized papers, plastic films, synthetic papers,
and metallic sheets, not to mention high-quality papers and coated papers. The invention provides novel
60 sheets for the ink jet recording, excelling in both ink jet recording properties and antistatic properties, which 60
are characterised in that the substrates are coated with a resin composition containing as the main
component an ultraviolet or radiation curing resin starting from natural high-molecular substances such as
casein, gelatin, starch base polysaccharides, cellulose derivatives, etc., and optionally including an (cationic,
anionic or ampholytic) ultraviolet or radiation curing antistatic agents, thereby to form an ultraviolet or
65 radiation-cured coating layer of said composition. 65

According to the first aspect of the present invention, there is obtained a sheet for the ink jet recording, excelling in both ink absorptivity and ink drying characteristics, and capable of providing colour copies of high picture quality, in which a substrate is coated with a formulation containing as the main component an ultraviolet or radiation curable resin starting from a natural animal or vegetable high molecular substance such as casein, gelatin, starch base polysaccharides, cellulose derivatives etc., and the thus coated layer is exposed to ultraviolet light or radiation beam, thereby to form a cross-linked coating layer serving as an ink receptor layer.

5

The ultraviolet or radiation curing casein, gelatin, starch base polysaccharides, cellulose derivatives and the like used in the present invention may be prepared by allowing a water-soluble high molecular compound to react with a compound containing a reactive double bond $>C=C<$ capable of effecting a cross-linking reaction by ultraviolet or radiation energy. The coating layer obtained by exposing the resin to ultraviolet light or radiation beam combines hydrophilic nature resulting from the starting substance with, at the same time, hydrophobic and water-resisting nature resulting from the cross-linking reaction. The thus obtained recording sheet excels in water base ink-receptivity and drying characteristics, in particular ink jet recording properties, and does not possibly undergo deformation such as surface waving at the printed portion which is often observed for ordinary and coated papers. The water absorption properties and drying characteristics of water base ink, the size and shape of ink dots, resolution and the water resistance of the surface recording layer depend upon the reactive double bond content of the ultraviolet or radiation curing resin forming the main component of the surface recording layer, or other compositions which are optionally added thereto, and comprise reactive or unreactive resins, and are determined depending upon the degree of cross-linking of the coated resin composition which is in turn determined by the ultraviolet or radiation exposure conditions. Consequently, the optimum recording layer in terms of the ink jet recording or the composition of ink is obtained through optimization of the aforesaid various conditions.

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In order to make an ink jet record having a high quality printed image with high resolution, according to the second aspect of the present invention, there is provided a recording sheet having a surface recording layer obtained by adding to (A) the aforesaid curing resin (B) an ultraviolet or radiation curing type antistatic agent having an ionic conductive property such as an acrylic cation resin including an ultraviolet or radiation curing type quaternary ammonium base or an acrylic anion resin including an ultraviolet or radiation curing type carboxylate group, and curing the resulting composition.

25

According to this aspect of the present invention, it is possible to obtain a printed image of high density and excellent resolution, since the acidic and basic dyes used in the water base ink for ink jet recording are prevented from longitudinal and cross-sectional diffusion into the recording layer by making use of the property that such dyes are selectively absorbed onto the ion radicals of the ultraviolet or radiation curing type antistatic agent.

30

The water base ink for ink jet recording contains as the main components dyes serving as colorants and a liquid medium for dissolving and dispersing them and, if necessary, may include wetting agents, binders, viscosity modifiers, bacteriostats and the like.

35

As the colorants use may be made of direct, acidic and basic dyes. For instance, when used is made of ink in which $-COOM$ or $-SO_3M$ (M is an alkali metal radical)-containing dyes are used, it is advantageous in view of recording performance to incorporate into the surface recording layer a cationic resin having an antistatic function.

40

The present invention has been accomplished based on the findings that extremely high picture quality is achieved by incorporating into the surface recording layer the ultraviolet or radiation curing antistatic agents based on its ionic conductive property.

The inventive sheets for water base ink recording, having the aforesaid features, are also best suited for drafting films by use of water base ink pens or for films for X-Y plotters using water base ink ball-points or felt pens.

45

Referring especially to the preparation of OHP transparent plastic sheets with the use of an X-Y plotter, it is now necessary to replace a colour water base ink pen used with normal paper by an oil base pen.

However, the recording sheet of the present invention makes possible the use of a conventional water base ink pen, and dispenses with any troublesome replacement of pens.

50

In addition, the inventive water base ink recording sheet having a coated layer containing the ultraviolet or radiation curing antistatic agent has antistatic properties and, when used with a backing substrate film, is dust-proof and does not offer any static handling problem.

Following is a description by way of example only of methods of carrying the invention into effect.

55

The starting materials of the animal or vegetable polymeric or high-molecular substances for the ultraviolet or radiation curing type resins used in the present invention include, for instance, casein, gelatin, starch base polysaccharides (dextrin, soluble starch, alpha starch, pulran, etc.) and their derivatives as well as cellulose derivatives (nitrocellulose, carboxymethyl-cellulose-CMC, methylcellulose-MC, hydroxy-
 5 propylmethylcellulose-HPMC, ethylcellulose-EC, hydroxyethylcellulose-HEC, hydroxypropylcellulose-HPC etc.). More specifically, the curing type resins include the following Chemical Substances I, II, III and IV starting from casein, gelatin, starch and CMC, as explained below in detail.

		<i>Starting Substance</i>	
10	Chemical Substance I (modified casein)	New Zealand Casein made by Fanleaf	10
15	Chemical Substance II (modified gelatin)	Gelatin P2115 made by Nitta Gelatin	15
	Chemical Substance III (modified starch)	Hydroxyethylated Potato starch trade name AVELEX 2530 made by AVEBE	
20	Chemical Substance IV (modified CMC)	Carboxymethylcellulose made by Sanyo Kokusaku Pulp	20

The starting substance gelatin for Chemical Substance II may be made water-resistant by using metallic salts containing a trivalent metal such as chromium, aluminium or ferric iron, aldehydes, ketones, quinones
 25 and the like. According to the present invention, however, use is made of the ultraviolet or radiation curing type gelatin obtained by modifying the amino, imino, hydroxy and carboxyl groups contained in the gelatin molecule with a chemical substance having groups capable of reacting with them, thereby introducing the ultraviolet or radiation-reactive double bonds $>C=C<$, grafting thereon a polymeric molecular chain having
 30 ultraviolet or radiation-reactive double bonds, or the like procedures. The thus obtained resin is exposed to ultraviolet light or radiation beam for crosslinking. Thus, the present invention makes it possible to provide an entirely novel, highly recordable sheet for ink jet recording by using the thus obtained water-resistant
 35 gelatin for a recording layer.

The procedures for preparing Chemical Substances I, II, III and IV involve the reactions between the relative starting materials casein, gelatin, starch, carboxymethylcellulose, etc., and (1) the epoxy groups of
 35 vinyl-epoxy compounds such as an allylglycidyl ether, styrylglycidyl ether, glycidyl acrylate, glycidyl methacrylate, glycidyl cinnamate and the like, (2) the carboxyl groups of vinylcarboxylic acids such as acrylic, methacrylic, cinnamic, crotonic and other acids, (3) the hydroxyl groups of vinyl-hydroxides such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate and
 40 the like, (4) the methylol groups of vinyl N-methylol compounds such as N-methylolacrylamide, N-methylolmethacrylamide, and the like, (5) the halogen radicals of allyl halides, halomethyl styrene, haloalkyl acrylates, haloalkyl methacrylates and the like, (6) the aziridine groups of vinylaziridine compounds
 45 such as aziridinoalkyl acrylates, aziridinoalkylmethacrylates and the like, (7) the aldehyde groups of acrolein, methacrolein and other compounds, etc.

The ultraviolet or radiation curing type antistatic agents having ionic/conductive properties according to
 45 the second aspect of the present invention includes, for example, acrylic cation resins having quaternary ammonium bases or acrylic anion resins having carboxylate groups. For instance, the following chemical substances V, VI and VII, etc. may be used.

Chemical Substance V: Acrylic cation resin having a quaternary ammonium base

Chemical Substance VI: Acrylic anion resin having an acrylate group

50 Chemical Substance VII: Carboxybetaine type acrylic ampholytic resin

Reference is made to the preparation of these Chemical Substances V, VI and VII. Referring to the purpose
 of illustration, the Substance V may be obtained by modifying with a haloalkyl acrylate an acrylic resin
 formed by the copolymerization of N, N-dimethylaminoethyl methacrylate with other monomer; the
 substance VI may be obtained by modifying with hydroxyethyl acrylate an acrylic resin formed by the
 55 copolymerization of acrylic acid with other monomer, followed by neutralization with an alkali; and the Substance VII may be obtained by modifying with a haloalkyl acrylate and a sodium monohaloacetate an
 60 acrylic resin formed by the copolymerization of N,N-dimethylaminoethyl methacrylate with other monomer.

The coating compositions, which form a recording layer of the inventive sheet for water base ink
 recording, particularly the sheet for ink jet recording, are composed mainly of (A) the ultraviolet or radiation
 65 curing type casein, gelatin, starch base polysaccharides or cellulose derivatives, and comprise optionally (B) an ultraviolet or radiation curing type antistatic agent. The kind and the amount of the ultraviolet or radiation
 curing type antistatic agent can be determined with the kind and the amount of the dyes used in ink.

In addition to the above-mentioned ultraviolet or radiation curing type resins (A) and (B), the recording
 layer-forming formulations may contain water-soluble, reactive monomers and oligomers which are
 65 polymerized and crosslinked upon exposure to ultraviolet light or radiation beam, and emulsion-based,

reactive resins as well as water-soluble, non-reactive high-molecular substances and resin components such as latexes and polyvinyl alcohol. Pigments, pigment dispersants, anti-foaming agents, UV absorbers and the like may be used.

The aforesaid resin formulations are coated by impregnation, size press, air knife, blade, bar, gravure, curtain, roll, spray or other like coatings, and the solvent is dried off, followed by exposure to ultraviolet light or electron beam, whereby the aforesaid ultraviolet or radiation curing type resin is polymerized and crosslinked to form a recording layer on the substrate sheet. The amount of the recording layer to be coated is in the range of 0.1 to 20 g/m², preferably 0.5 to 10.0 g/m². The substrate sheet used may be paper with controlled degree of sizing, air permeability and smoothness, processed paper having a barrier coating layer of resin or an extruded coating layer of thermoplastics, coated papers, cast papers, resin impregnated papers, papers containing synthetic fibers, synthetic pulp and inorganic fibers, metallized papers, synthetic papers, plastic films, metal films and the like.

For ultraviolet or radiation curing, use may be made of any one of ultraviolet lights emanating from, e.g., a high pressure mercury lamp, electron beam and gamma ray.

When using ultraviolet light, 0.5 to 5.0 weight parts of initiator for photo-induced cross-linking reaction are added to 100 weight parts of the ultraviolet curing type resin composition. The photo-initiators used may include ketones, benzoines, quinones, thioxantones, triazoles, salicylic acids or other known agents. Optionally, sensitizers may be employed. Such additives may not be necessary for electron beam curing.

In what follows, the present invention will now be explained in further detail with reference to the following non-restrictive examples, in which the term "part" shall refer to "part by weight", unless otherwise specified.

(A) Preparation of the Ultraviolet or Radiation Curing Type Resin

25 *Chemical Substance I* (modified casein) 25

100 parts of casein produced in New Zealand and processed by Fanleaf Co., Ltd. and 350 parts of a mixed water-isopropanol solvent (50 : 50 weight ratio) were charged in a flask, while they were stirred at 40°C. To the flask 2 parts of potassium hydroxide were added, and the resulting mixture was stirred for 30 minutes. Thereafter, 30 parts of glycidyl acrylate and 1 part of zinc oxide were further added, and the resultant mixture was heated to 60°C, at which it was stirred for further 30 hours to obtain Chemical Substance I.

Chemical Substance II (modified gelatin)

100 parts of gelatin (manufactured by Nitta Gelatin Co., Ltd. and sold under the trade name of P2115) were charged with 200 parts of 1,4-dioxane in a flask, while they were stirred at 60°C. To the flask 15 parts of acrylic acid and 0.5 part of p-toluenesulfonic acid were added, and the resulting mixture was stirred for further 20 hours, followed by the addition of 150 parts of water, thereby to obtain Chemical Substance II.

40 *Chemical Substance III* (modified starch) 40

100 parts of hydroxyethylated potato starch (manufactured by AVEBE Co., Ltd. and sold under the trade name of AVELEX 2530) and 400 parts of a mixed water-isopropanol solvent (60 : 40 weight ratio) were charged into a flask, while they were stirred at 50°C. To the flask 10 parts of glycidyl cinnamate and 0.3 part of tetramethylammonium bromide were added, and the resulting mixture was stirred for further 15 hours to obtain Chemical Substance III.

Chemical Substance IV (modified CMC)

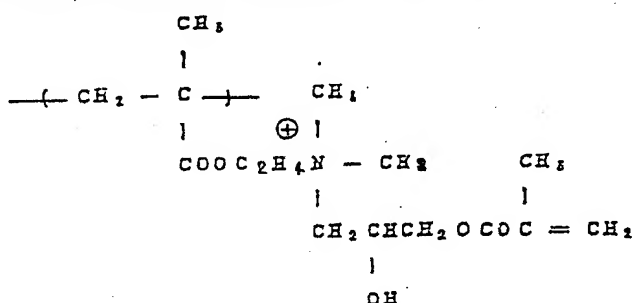
100 parts of carboxymethylcellulose manufactured by Sanyo Kokusaku Pulp Co., Ltd. and 900 parts of a mixed water-isopropanol solvent (50 : 50 weight ratio) were charged into a flask, while they were stirred at 40°C. To the flask 5 parts of sodium hydroxide were added, followed by stirring for 30 minutes. Thereafter, 20 parts of 3-chloro-2-hydroxypropyl methacrylate were added, and the resulting solution was heated to 60°C, at which it was stirred for further 25 hours to obtain Chemical Substance IV.

(B) Preparation of the Ultraviolet or Radiation Curing Type Antistatic Agents

Chemical Substance V (Acrylic cation resin including quaternary ammonium base)

50 parts of N,N-dimethylaminoethyl methacrylate, 50 parts of methyl methacrylate, 100 parts of isopropanol and 0.5 part of 2,2'-azobisisobutyronitrile were charged into a flask, in which they were polymerized for 6 hours at 30°C in a nitrogen atmosphere. The reaction product was then ice-cooled, to which 57 parts of 3-chloro-2-hydroxypropyl methacrylate and 250 parts of water were added dropwise. The thus prepared solution was stirred for 1 hour and then at 50°C for 3 hours to obtain Chemical Substance V.

In its molecular chain, this acrylic polymer (hereinafter referred to as Chemical Substance V) includes:

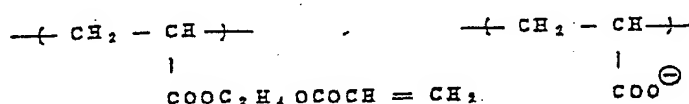


Chemical Substance VI

15 (Acrylic anion resin including acrylate group)

50 parts of acrylic acid, 50 parts of ethyl acrylate, 100 parts of 1,4-dioxane and 0.5 part of 2,2'-azobisisobutyronitrile were charged into a flask, in which they were polymerized for 6 hours at 80°C in a nitrogen atmosphere. Thereupon, 40 parts of 2-hydroxyethyl acrylate and 1.5 part of p-toluenesulfonic acid were added to the reaction product, and the resulting solution was stirred for 4 hours at 50°C and ice-cooled, followed by dropwise addition of 14 parts of sodium hydroxide and 240 parts of water. The thus obtained solution was stirred for 1 hour and then at 40°C for further 3 hours to obtain Chemical Substance VI.

In its molecular chain, this acrylic polymer (hereinafter referred to as Chemical Substance VI) includes:

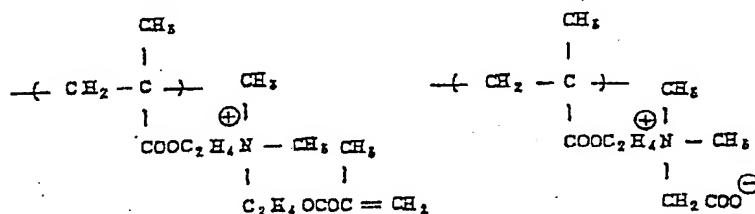


Chemical Substance VII

30 (Carboxybetaine type acrylic ampholytic ion resin)

60 parts of N,N-dimethylaminoethyl methacrylate 40 parts of butyl methacrylate, 100 parts of isopropanol and 0.5 part of 2,2'-azobisisobutyronitrile were charged into a flask, in which they were polymerized for 6 hours at 80°C in a nitrogen atmosphere. After ice-cooling, 28 parts of 2-chloroethyl methacrylate and 130 parts of water were added dropwise to the reaction product, and the whole was agitated for 1 hour and then at 50°C for 3 hours. After further ice-cooling, 22 parts of sodium monochloroacetic acid and 100 parts of water were added dropwise to the mixture, and the solution was stirred for 1 hour and then at 40°C for further 3 hours to obtain Chemical Substance VII.

In its molecular chain, this acrylic polymer (hereinafter referred to as Chemical Substance VII) includes:



Example 1

Preparation was first made of a solution of 10 weight % of a composition in a mixed water/isopropanol (50 : 50 weight ratio) solvent, said composition consisting of 100 weight parts of the ultraviolet curing type casein (Chemical Substance I) and 3 weight parts of an initiator manufactured by Stauffer Co., Ltd. and sold under the trade name of Vicure 55. This solution was coated onto a polyester film (100 microns) by means of a Meyer bar in such a manner that its content amounted to 2.0g/m² in terms of dried solid, said film being previously coated with an anchor coating agent manufactured by Toyo Ink Seizo Co., Ltd. and sold under the trade name of Under Lacquer RU, 0.5 g/m². After drying, ultraviolet light was irradiated on it at a conveyor speed of 10 m/min. with the use of an ultraviolet curing apparatus (made by Ushio Denki Co., Ltd. and commercially available under the trade name of Unicure 4000, 160 W/cm) to prepare a transparent film for ink jet recording, including a set recording layer.

Example 2

Preparation was first made of a 10 weight % solution of a composition in a mixed water/isopropanol (50 : 50 weight ratio) solvent, said composition consisting of 100 weight parts of the ultraviolet curing type gelatin (Chemical Substance II) and 3 weight parts of an initiator available under the trade name of Vicure 55 (manufactured by Stauffer Co., Ltd.). This solution was coated onto a polyester film which had already been undercoated as described in Example 1, with the use of a Mayer bar in such a manner that its content amounted to 4.0 g/m² in terms of dried solid. After drying, ultraviolet light was irradiated (at a conveyor speed of 10 m/min.) to prepare a transparent film for ink jet recording, including a set recording layer.

10 *Example 3*

A composition was first prepared consisting of the ultraviolet curing type casein (Chemical Substance I) and the ultraviolet curing type cationic antistatic agent (Chemical Substance V) in a solid proportion of 75 : 25. Preparation was then made of a solution of a 10 weight % formulation in a mixed water/isopropanol (50 : 50 weight ratio) solvent, said formulation consisting 100 weight parts of said composition and 3 weight parts of an initiator available under the trade name of Vicure 55 (manufactured by Stauffer Co., Ltd.). This solution was coated onto a polyester film which had been undercoated as described in Example 1, in such a manner that its content amounted to 4.0 g/m² in terms of dried solid. After drying, ultraviolet light was irradiated (at a conveyor speed of 10 m/min.) to prepare a set recording layer-containing transparent sheet of ink jet recording in which the ultraviolet curing type cationic antistatic agent was used.

20 *Examples 4 and 5*

In place of the ultraviolet curing type cationic antistatic agent (Chemical Substance V) use was made of ultraviolet curing type anionic antistatic agent (Chemical Substance VI) and the ultraviolet curing type amphoteric antistatic agent (Chemical Substance VII). These agents were combined with the ultraviolet curing type casein (Chemical Substance I) in a proportion similar to that applied in Example 3, and were formulated with an initiator similar to that used in Example 3. From the obtained formulations, the transparent films for ink jet recording of Examples 4 and 5 were prepared according to Example 3.

Example 6

10 weight % solutions of the radiation curing type casein (Chemical Substance I) and the radiation curing type gelatin (Chemical Substance II) in a mixed water/isopropanol (50 : 50 weight ratio) solvent were respectively coated onto the previously undercoated polyester films, as used in Example 1, by means of a Mayer bar in such a manner that their content amounted to 4.0 g/m² in terms of dried solid. Thereafter, the films were exposed to 1.0 Mrad of electron beam at an acceleration voltage of 150 KV and a beam current of 2.0 mA with the use of an electron beam irradiation apparatus (Electron Curtain CB 150/15/10 L manufactured by Energy Science Co., Ltd) to obtain set recording layers. In this manner the transparent films (Ex. 6A and 6B) for ink jet recording were obtained.

Example 7

Preparation was first made of a 10 weight % solution of a composition in a mixed water/isopropanol (50 : 50 weight ratio) solvent, said composition consisting of 100 weight parts of the ultraviolet curing type casein (Chemical Substance I) and 3 weight parts of an initiator available under the trade name of Vicure 55 (manufactured by Stauffer Co., Ltd). This solution was coated onto the coated paper (SK Coat, tradename, manufactured by Sanyo Kokusaku Pulp Co., Ltd.) by means of a Mayer bar in such a manner that its content amounted to 4.0 g/m² in terms of dried solid. Thereafter, the paper was exposed to ultraviolet light at a conveyor speed of 10 m/min. to obtain a paper based sheet for ink jet recording.

The sheets of Examples 1 - 7, a commercially available high-quality paper for ink jet recording (Comparative Example 1) and the coated paper used in Example 7 (Comparative Example 2) were estimated on their ink jet recording performance in the following manner.

50 1. Measurement of Dot Optical Density and Diameter: measured by using Sakura Densitometer PDM-5 (manufactured by Konishiroku Kogyo Co., Ltd.)

2. Observation of Dot Shape: observed by using a microscope

O Sharply contrasted round shape

Δ Round shape

55 X Distorted not round shape

3. Drying Rate of Ink: Measured by using Ink Jet Color Printer IO-0700 (manufactured by Sharp Co., Ltd.).

When recording a test pattern, a sheet-keeping roller was placed on an imaged portion. Just after recording, the roller was fed forward to measure a stain in mm resulting from an undried amount of ink.

60 4. Surface Resistivity: Measured at 20°C 65% RH with the use of Terao Meter, trade name, (manufactured by Kawaguchi Denki Co., Ltd.)

5. Water Resistance: A certain amount of water was added dropwise onto the coated film and, just thereafter, was wiped out to measure the degree of damaging thereof.

O: Not damaged

Δ: Somewhat damaged

65 X: Entirely wiped out

The results are shown in Table 1.

TABLE 1

5 Samples	Dot Shape	Dot Diameter in μm	Dot Optical Density (Black)	Drying Rate of Ink (mm)	Surface Resistivity (Ω)	Water Resistance	5
Example 1	O	160	1.82	5	3.8×10^{12}	0	10
10 Example 2	O	170	1.80	0	4.5×10^{14}	0	
Example 3	O	200	1.78	0	6.3×10^{10}	0	
Example 4	O	204	1.50	7	1.1×10^{11}	0	
Example 5	O	210	1.72	0	2.3×10^{11}	0	
Example 6 (A)	O	165	1.82	0	4.1×10^{12}	0	15
15 Example 6 (B)	O	170	1.80	0	5.2×10^{14}	0	
Example 7	O	160	1.78	5	2.8×10^{12}	0	
Comparative Ex. 1 High Quality Paper	X	310	1.10	0	7.2×10^{11}	-	20
20 Comparative Ex. 2 Coated Paper	Δ	280	1.70	13	6.5×10^{12}	-	

The transparent sheets for ink jet recording according to Examples 1 - 5, 6A and 6B of the present invention were printed with the use of an ink jet color printer (IO-0700 manufactured by Sharp Co., Ltd). As a result, it was found that the drying properties of the water base ink was good, and the printed portion was so good that it was not rubbed off at all. In addition, the printed image was of high color optical density, was clear and had a high resolution, so that it was best suited for use as a color OHP film. The ink jet recording paper of Example 7 provided a clear printed image of high color density and high resolution. Compared with the coated paper (Comparative Example 2) and the ink jet recording paper of high quality (Comparative Example 1), that sheet was of much higher picture quality.

The recording sheet of Example 1 according to the present invention was used for drawing with a water base ink pen (black, red, green, blue) by means of an X-Y plotter PL-2000 (manufactured by Yokokawa Electric Works Co., Ltd.). It was found that the drawn lines of various colors were excellent, and the drying properties of the ink was good. Ink adhesion was also good enough not to be rubbed off. Thus, that sheet was best suited for use as an OHP film.

CLAIMS

1. A sheet material for use in ink jet recording or printing comprising a substrate having a layer including a radiation, curable resin of high molecular weight which has been cured to form a cross-linked coating having an ink receptor surface.
2. A material as claimed in claim 1 wherein the radiation curable resin is curable by at least one of ultraviolet radiation, alpha, beta or gamma particle radiation.
3. A material as claimed in claim 1 or claim 2 wherein the resin is of animal or vegetable origin.
4. A material as claimed in claim 3 wherein the resin comprises one or more of casein, gelatin, starch based polysaccharides, and cellulose derivatives.
5. A material as claimed in any preceding claim wherein the resin is a radiation curable antistatic agent having an ionic conductive property.
6. A material as claimed in claim 5 wherein the antistatic agent is selected from acrylic cation resins having a quaternary ammonium base and acrylic anion resins having a curable carboxylate group.
7. A sheet as claimed in any preceding claim wherein the resin includes water soluble reactive monomers and oligomers which are capable of polymerisation and/or crosslinking upon exposure to said radiation.
8. A sheet as claimed in any preceding claims wherein the resin includes emulsion based reactive resins, water soluble non-reactive high molecular substances, pigments, pigment disperants, anti-foaming agents and UV absorbers.
9. A sheet as claimed in any one of the preceding claims including 0.5 to 5% by weight of photo-initiator.
10. A sheet as claimed in any preceding claim wherein the coating of the substrate is in the range 0.1 to 20 gm/m².
11. A sheet as claimed in any preceding claim wherein the substrate is selected from paper, coated paper, cast paper, resin impregnated papers, papers containing synthetic fibers, papers containing synthetic pulp and/or inorganic fibers, plastic films and metal films.
12. A sheet as claimed in claim 1 and substantially as described in any one of the specific examples herein set forth.

13. A method of making a sheet material as claimed in any one of the preceding claims which method comprises preparing the radiation curable resin composition applying said composition to the substrate and subjecting said composition to radiation to effect curing of said resin composition.
14. A method as claimed in claim 13 wherein the resin composition is applied by impregnation, size press, air knife, blade, bar, gravure, curtain, roll or spray. 5
15. A method as claimed in claim 13 or claim 14 wherein the amount of resin composition applied to the substrate is in the range 0.1 to 20 gm/m².
16. A printed sheet comprising the sheet material claimed in any one of claims 1 to 12 having ink thereon applied by ink jet.
- 10 17. A printed sheet as claimed in claim 16 wherein the ink is a water base ink. 10
18. A printed sheet as claimed in claim 17 wherein the ink contains dyes and one or more of wetting agents, binders, viscosity modifiers and bacteriostats.
19. A sheet for water base ink recording, in which a backing substrate includes a surface layer obtained by ultraviolet or radiation curing of a composition composed mainly of an ultraviolet or radiation curing type resin starting from a natural high-molecular substance. 15
20. A sheet for water base ink recording, in which a backing substrate includes a surface resin layer obtained by ultraviolet or radiation curing of a composition composed mainly of (A) an ultraviolet or radiation curing type resin starting from a natural high-molecular substance and containing (B) an ultraviolet or radiation curing type antistatic agent.
- 20 21. Each and every novel embodiment herein set forth taken either separately or in combination. 20

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